

# The ab-initio calculation of crystal structure and lattice dynamics of perfect and defective MeX ( $\text{Me}^+ = \text{Rb}^+, \text{K}^+, \text{Na}^+$ ; $\text{X}^- = \text{F}^-, \text{Cl}^-$ )

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**Abstract.** In this work, the interionic pair potentials  $\text{X}^- - \text{X}^-$ ,  $\text{Me}^+ - \text{X}^-$  ( $\text{Me}^+ = \text{Rb}^+, \text{K}^+, \text{Na}^+$ ;  $\text{X}^- = \text{F}^-, \text{Cl}^-$ ) within the framework of shell model were obtained using the self consistent field Roothaan-Hartree-Fock approximation allowing the correlation correction in second order Moller-Plesset form. Further, nonempirical pair potentials were used for the calculations of the structure and lattice dynamics of perfect and imperfect alkali halides crystals. Impact analysis of anion vacancies influence on crystal vibrational spectrum was carried out with the help of recursive technique calculations of symmetrized and localized density of vibrational states in the perfect and vacancies including crystal.

## 1. Introduction

Interest in alkali metal halides crystals is caused by ample opportunities of technical applications of these crystals. Moreover, the simple structure of these crystals allows their use as convenient objects for testing various theoretical models.

Point defects existing at these crystals even in a low concentration have a significant effect, e.g., on lattice dynamics, which is manifested in various defect-related processes. Therefore, the study of these processes requires information on the influence of defects on the lattice structure and dynamic characteristics. This information, in many cases, can be obtained only from numerical simulations.

The conventional approach using the shell model in the pair-interaction approximation [1, 2] has shown its efficiency in the description of the structure and lattice dynamics of pure crystals and in the description of the effect of defects and impurities [3]. This approach is physically clear and simple and allows highly accurate description of long-range electrostatic contributions and long-range electrostatic screening.

In this paper, a nonempirical method is used to determine the parameters of pair interionic potentials for crystals of a number of alkali metal halides and these potentials are then used to describe the structure and dynamics of perfect and imperfect crystal lattices.

## 2. Model for calculating the energy of ionic crystal

As noted above, a rigorous calculation of the structure and dynamics of the lattice of an ionic crystal with defects by any a nonempirical method is currently impossible. Therefore, we use the

shell model in the approximation of pair interionic potentials. In this approach, the interaction energy  $U_{km}$  of an ion pair is given by

$$U_{km} = \frac{X_k X_m}{r} + \frac{Y_k X_m}{|\mathbf{r}_{km} + \mathbf{l}_k|} + \frac{X_k Y_m}{|\mathbf{r}_{km} - \mathbf{l}_m|} + \frac{Y_k Y_m}{|\mathbf{r}_{km} + \mathbf{l}_k - \mathbf{l}_m|} + \frac{1}{2}(K_k l_k^2 + K_m l_m^2) + \varphi(r) \quad (1)$$

where  $X$  and  $Y$  are the charges of the core and electron shell, respectively;  $K$  is the coreshell elastic interaction constant;  $r = |\mathbf{r}_{km}|$  is the distance between the ion pair cores;  $\mathbf{l}_k$  is the displacement of the shell with respect to its core; and  $\varphi(r)$  is the pair short-range interaction potential. We used the short-range interaction

$$\varphi(r) = \sum_{i=1}^n C_{km}^{(i)} \exp\left(-\frac{r}{D_{km}^{(i)}}\right) - \frac{\lambda_{km}}{r^6} \quad (2)$$

where the first term is the repulsive exchange interaction between two ions and the second term is the van der Waals interaction.

To determine the shell charge, we use a test-charge method [9].

### 3. Results and discussion

#### 3.1. Calculation of the Model Parameters

At the first stage of calculations, we determined the polarizabilities  $\alpha$  of free ions and the effective charges  $Y$  of their electron shells, which define the interaction constants  $K$  of ion cores and shells  $K = Y^2/\alpha$ . Having performed a quantum-mechanical calculation of the dipole moment  $\mathbf{p} = \alpha \mathbf{E}$  induced by a uniform electric field  $\mathbf{E}$  using the HFR method, we determined the linear polarizability  $\alpha$  (which is a second-rank tensor in general). This approach is implemented in the PC GAMESS (US) software package (a set of quantum-mechanical computer programs) [6].

The effective shell charge  $Y$  was calculated using a test-charge method in which two point charges  $q$  are arranged symmetrically at a distance  $r$  from the ion on a straight line passing through the ion.

As in the previous case, the tensor components  $\alpha_{\beta\gamma}$  are calculated from first principles. By calculating the polarizability on a fixed grid of  $r$  and  $q$  values, we obtained a set of points defining the  $\alpha_{\beta\beta}(r, q)$  dependence. In the shell model, the polarizability  $\alpha_{\beta\beta}(r, q)$  is given by

$$\alpha_{xx}(r, q) = Y^2 \left/ \left( \frac{Y^2}{\alpha_0} + 4 \frac{qY}{r^3} \right) \right., \quad (3)$$

$$\alpha_{zz}(r, q) = \alpha_{yy}(r, q) = Y^2 \left/ \left( \frac{Y^2}{\alpha_0} - 2 \frac{qY}{r^3} \right) \right. \quad (4)$$

where  $\alpha_0$  is the ion polarizability in the absence of external charges. We calculated only one component of  $\alpha_{\beta\beta}(r, q)$  in the shell model and determined the  $Y$  values optimally reproducing the calculated nonempirical polarizability  $\alpha_{\beta\beta}(r, q)$ .

In order to determine the parameters of the pair potentials of the  $X^-$ - $X^-$  short-range interaction, we calculated the ground-state energy of the  $[X_2]^{2-}$  cluster of two  $X^-$  ions at various distances between the nuclei. The parameters were determined by the least squares method from the best fit of the numerically calculated energy to its model expression.

The short-range interaction potential of  $Me^+$ - $F^-$  ions was determined from calculating the energy of the symmetric  $[MeX_2]^{-1}$  cluster. The pair interaction parameters were also determined by the least squares method from the best fit of the numerically calculated energy to its model expression.

All the calculations were carried out using the following sets of Gaussian atomic basis functions: cc-pVQZ [7] for halide atoms and Sadlej pVTZ [8] for metal atoms.

The calculated interionic potential parameters, shell charges, and coreshell elastic interaction constants are listed in Table 1. Interionic potential parameters for  $Me^+F^-$  were published [9].

**Table 1.** Parameters of the short-range part of ion interaction potential, shell charges  $Y$ , and elastic constants  $K$ 

Interacting ions	$C_{km}^1$ , eV	$D_{km}^1$ , eV/Å	$C_{km}^2$ , eV	$D_{km}^2$ , eV/Å	$\lambda_{km}$ , eV/Å <sup>6</sup>	Ion	$Y$ ,  e <sup>-</sup>	$K$ , eV/Å <sup>2</sup>
Rb <sup>+</sup> -Cl <sup>-</sup>	2389.70	0.322	4874.26	0.282	—	Rb <sup>+</sup>	-5.54	352.8
K <sup>+</sup> -Cl <sup>-</sup>	1412.35	0.311	5240.53	0.280	—	K <sup>+</sup>	-4.08	305.8
Na <sup>+</sup> -Cl <sup>-</sup>	333.44	0.312	1912.63	0.300	—	Na <sup>+</sup>	-1.93	422.1
Cl <sup>-</sup> -Cl <sup>-</sup>	6747.14	0.306	94.72	0.498	378.46	Cl <sup>-</sup>	-5.00	190.2

### 3.2. Calculation of the properties of $Me^+X^-$ ( $Me^+ = Rb^+, K^+, Na^+$ ; $X^- = F^-, Cl^-$ ) crystals with perfect lattice

To validate the calculated ion interaction potentials, various physical parameters were calculated for the  $Me^+X^-$ . In Table 2, we give the lattice constant  $a$ , the elastic constants  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  calculated for the crystal lattice at equilibrium, as well as the experimental data (dataset for  $Me^+F^-$  can be found in [9]).

**Table 2.** Physical parameters of the perfect  $Me^+Cl^-$  crystals ( $Me^+ = Rb^+, K^+, Na^+$ )

Quantity	RbCl		KCl		NaCl	
	calculation	experiment	calculation	experiment	calculation	experiment
$a$ , Å	6.55	6.60[10]	6.22	6.29[10]	5.70	5.64[10]
$C_{11}$ , GPa	43.06	42.97[11]	53.67	39.81[12]	64.44	57.33[11]
$C_{12}$ , GPa	6.18	6.49[11]	7.73	6.10[12]	12.08	11.23[11]
$C_{44}$ , GPa	6.18	4.93[11]	7.73	6.32[12]	12.08	13.31[11]
$\nu_{TO}(\Gamma)$ , THz	3.5	3.7[10]	4.5	4.3[10]	5.3	4.9[10]
$\nu_{LO}(\Gamma)$ , THz	5.8	5.2[10]	7.2	6.4[10]	9.0	7.9[10]

We can see that, in general, almost all physical parameters are described satisfactorily. Table 2 also lists the calculated frequencies  $\nu_{TO}(\Gamma)$  and  $\nu_{LO}(\Gamma)$  of the transverse and longitudinal optical vibrations, respectively, and compares them with the experimental data.

### 3.3. Atomic structure and lattice dynamics near anion vacancies in the $Me^+X^-$ crystals ( $Me^+ = Rb^+, K^+, Na^+$ ; $X^- = F^-, Cl^-$ )

In order to describe the static lattice deformation near anion vacancies and the polarization of crystal regions far from anion vacancies, we used the molecular-statics method [13].

The displacements of the first and third nearest neighbors are directed away from the vacancy, while the second nearest neighbors are displaced toward the vacancy. The displacements of ions in various crystals differ only in magnitude. The calculations show that the ion displacements outside the third CS oscillate and decay slowly with distance from the vacancy. This character of the lattice distortion indicates that the perturbation is strong and is not localized in a small region.

When calculating the the symmetrized vibrational local density of states (VLDOS) by the recursive method, the initial vectors were taken to be symmetrized ion displacements in the first

two CSs of the  $X^-$  ion that was then replaced by an anion vacancy. The center of these CSs is characterized by point group  $O_h$ .

**Table 3.** Frequencies in THz of defect vibrations induced by vacancies in the  $Me^+Cl^-$  crystals ( $Me^+ = Rb^+, K^+, Na^+$ )

Vibration symmetry	RbCl	KCl	NaCl
$A_{1g}$	1.6; 4.0; 5.1	2.3; 3.2; 5.3; 5.8	3.0; 3.8; 7.4; 8.1
$E_g$	1.4; 3.2; 3.8; 5.1	1.8; 6.3	2.5; 3.3; 7.7
$T_{2g}$	1.5	1.7; 4.6	2.5; 4.8
$T_{1u}$	3.8; 5.1	5.1; 6.4	4.8; 7.3; 7.8

In the first-order IR absorption spectra of crystals with defects whose position symmetry is described by group  $O_h$ , the  $T_{1u}$  vibrations are IR active, according to group theory. The Raman-active vibrations are only the  $A_{1g}$ ,  $E_g$  and  $T_{2g}$  modes. Hence, interpretation of the experimental IR absorption and Raman spectroscopy data requires information on the vibrational density of states for the  $T_{1u}$  mode and the densities of states averaged over all possible combinations of the  $A_{1g}$ ,  $E_g$  and  $T_{2g}$  modes. Therefore, these symmetrized VLDOSs were of most interest.

After calculating the symmetrized VLDOS for perfect and imperfect crystals using the entire set of coordinates of the  $A_{1g}$ ,  $E_g$ ,  $T_{2g}$  and  $T_{1u}$  modes, we calculated the frequencies of localized vibrations induced by vacancies in  $Me^+X^-$  crystals. The frequencies for  $Me^+Cl^-$  are listed in Table 3 (frequencies for  $Me^+F^-$  are listed in [9]).

#### 4. Conclusion

We have proposed a method for determining the parameters of the shell model and pair interionic potential approximation from ab initio calculations of the cluster electronic structure with direct inclusion of the correlation effects. It has been shown that this method can be reliably applied to calculations of the lattice structure and dynamics of perfect ionic crystals and ionic crystals with point charged defects.

The constructed scheme for determining the model parameters is universal and applicable to calculations of the properties of more complex crystals.

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